

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-139304

(43)Date of publication of application : 22.05.2001

(51)Int.Cl.

C01B 3/38

C01B 3/56

// H01M 8/06

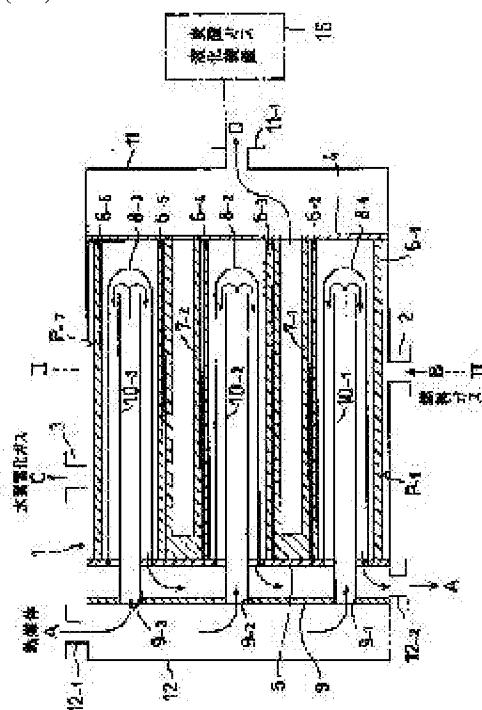
(21)Application number : 11-317904

(71)Applicant : TOSHIBA CORP

(22)Date of filing : 09.11.1999

(72)Inventor : OGATA TOMOKO
FUKUDA MASAFUMI

(54) CARBON DIOXIDE SEPARATION TYPE REFORMER



(57)Abstract:

PROBLEM TO BE SOLVED: To unnecessitate a large-scaled device by separating carbon dioxide while reforming methane into a hydrogen enriched gas.

SOLUTION: Plural sections are formed by dividing the inside of a tightly closed drum part in a fluid tight state with a reforming catalyst layer for reforming methane to convert into the hydrogen enriched gas, a heating tube group, through which the heating medium is passed, and a porous ceramic pipe group impregnated with zirconate to permeate only carbon dioxide are arranged in the sections adjacent to each other. A fuel gas prepared by mixing methane with steam is heated by the heating pipes and passed through plural reforming catalyst layers to perform the reforming reaction to obtain the hydrogen enriched gas and carbon dioxide simultaneously produced is taken out through the

porous ceramic pipe to be recovered.

FULL CONTENTS

[Claim(s)]

[Claim 1] The reforming catalyst layer which converts into hydrogen enriched gas the heating gas which mixed the steam with methane while holding in the sealed idiosoma and this idiosoma, dividing a core and forming two or more blocks, Porous body ceramic tubing which infiltrates the heating tube and JIRUKONEITO for pouring the heat carrier stored by turns into the adjoining block separated by this reforming catalyst layer, and makes only carbon dioxide gas penetrate, The header for heat carriers for being prepared in said idiosoma and circulating a heat carrier to said each heating tube, The header for carbon-dioxide-gas recovery for collecting the carbon dioxide gas obtained by being prepared in said idiosoma and penetrating said each porous body ceramic tubing, The carbon-dioxide-gas discrete type refining machine which consists of the heating gas entrance part prepared in order to supply said heating gas to the block divided by said reforming catalyst layer, and the hydrogen-enriched-gas Deguchi part prepared in order to collect hydrogen enriched gas.

[Claim 2] Said heating tube is a carbon-dioxide-gas discrete type refining machine according to claim 1 characterized by considering it as the hollow dual structure which consists of a container liner and a long and slender test tube type outer case.

[Claim 3] Said heating tube is the carbon-dioxide-gas discrete type refining machine according to claim 1 which uses the heating tube of a U tube format.

[Claim 4] The carbon-dioxide-gas discrete type refining machine according to claim 1 characterized by having made the header for carbon-dioxide-gas recovery open for free passage, and establishing a decreased pressure means to make a ceramic tubing internal pressure lower than a ceramic tubing external pressure.

[Claim 5] It is the carbon-dioxide-gas discrete type refining machine according to claim 4 characterized by constituting said decreased pressure means from a carbon-dioxide-gas liquefier.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the carbon-dioxide-gas discrete type refining machine which does not discharge the carbon dioxide gas reformed and generated with respect to a fuel refining machine.

[0002]

[Description of the Prior Art] if methane is reformed conventionally -- hydrogen -- while becoming ***** gas, carbon dioxide gas is generated. However, since [leading to global warming] the matter, it is necessary to process carbon dioxide gas so that it may not be emitted into the air. Moreover, the methane reforming reaction became one condition for holding temperature at about 800 degrees C or more to obtain the greatest rate of refining, and there was a problem that energy expenditure increased.

[0003]

[Problem to be solved by the invention] The above-mentioned conventional technique cannot separate the carbon dioxide gas generated by refining, but will be emitted into the

air. However, since [leading to global warming] the matter, it is necessary to process carbon dioxide gas so that it may not be emitted into the air.

[0004] As this invention can also separate carbon dioxide gas in view of the above-mentioned problem, carrying out methane refining, it offers the carbon-dioxide-gas separation refining machine which made large-scale equipment unnecessary.

[0005]

[Means for solving problem] In order to attain the above-mentioned object, divide with the reforming catalyst layer which reforms methane and converts the inside of the sealed idiosoma into hydrogen enriched gas in the fluid-tight condition, and this invention forms two or more blocks. Porous body ceramic tubing which infiltrates the heating tube and JIRUKONEITO for pouring a heat carrier, and makes only carbon dioxide gas penetrate is arranged to an adjoining block. While heating the heating gas which mixed methane and a steam with a heating tube, when making two or more reforming catalyst layers penetrate, it constitutes so that a reforming reaction may be made to perform and hydrogen enriched gas may be obtained.

[0006] By adopting such architecture, it can process so that carbon dioxide gas may not be emitted. Moreover, advancing the reforming reaction of methane, by separating carbon dioxide gas, a methane reforming reaction equilibrium collapses and a reforming reaction is promoted.

[0007]

[Mode for carrying out the invention] The architecture of this invention is hereafter explained in detail based on the form of operation shown in drawing 1 , drawing 2 , and drawing 3 .

[0008] Drawing 1 is a sectional view when it being perpendicular and cutting the carbon-dioxide-gas separation refining machine concerning this invention. In addition, drawing 2 is a sectional view which meets the II-II line of drawing 1 .

[0009] 1 is tubed idiosoma which stores various kinds of equipment required for refining, and components, and is installing the hydrogen-enriched-gas outlet pipe 3 which takes out the hydrogen enriched gas which mentions later the combustion gas inlet tubing 2 with which combustion gas A which mixed the steam with methane in the graphic display lower part of this idiosoma flows in the graphic display upper part again, and which was reformed and obtained. And a tube sheet 4 is attached to the graphic display right-hand side opening end of this idiosoma 1, and the tube sheet 5 is attached to the graphic display left-hand side opening end, respectively. In addition, the expedient upper joint plate 4 of description is called the 1st tube sheet, and a tube sheet 5 is called the 2nd tube sheet. As drawing 2 (A) shows, the reforming catalyst layer 6-1 of six layers which divides the pass from the combustion gas inlet tubing 2 to the hydrogen-enriched-gas outlet pipe 3 into seven blocks P-1 and P-2--P-7, 6-2, --6-6 are provided in the portion surrounded with said idiosoma 1, the 1st tube sheet 4, and the 2nd tube sheet 5. This reforming catalyst layer 6-1, 6-2, --6-6 are filled up with the reforming catalyst which produces an endothermic reaction when converting into hydrogen enriched gas heating gas A which mixed the steam with methane.

[0010] In addition, as drawing 2 (B) shows to said 1st tube sheet 4, it opens a pore 4-1 and four 4-2 in the block P-3 between two-layer [of a reforming catalyst layer / three layers of] and the four-layer block P-5 for five layers, and a corresponding location at a time, respectively. The periphery part of the cylindrical ceramic tubing 7 which closed

these pores 4-1 and a bottom as shown in the periphery part of 4-2 by drawing 3 is attached airtightly. Moreover, shock absorbing material 4A is provided in the portion which a tube sheet 4 and the ceramic tubing 7 contact so that clearly from drawing 3. Thus, the ceramic tubing 7 is being fixed to the 1st tube sheet 4, where it faced opening the pore 4-1 of the 1st tube sheet 4, and 4-2 and a bottom is turned to the 2nd tube sheet 5. This ceramic tubing 7 infiltrates JIRUKONEITO (following chemical formula 1), and is constituted as a porous body which can pass only carbon dioxide gas.

[0011] [-izing 1]

As drawing 2 (C) shows to LiZrO₃ one side and said 2nd tube sheet 5 The block P-2 between one-layer two-layer [of a reforming catalyst layer], and the three-layer block P-4 for four layers, It opened a pore 5-1, 5-2, and four 5-3 in the five-layer block P-6 for six layers, and the corresponding location at a time, respectively, and the periphery part of the heating tube 8-1 of the shape of a test tube which is equivalent to opening of these pores 5-1, 5-2, and 5-3 at the outer case of a double pipe, 8-2, and 8-3 is attached. That is, where a bottom is turned to the 1st tube sheet 4, the heating tube 8 is being fixed to the 2nd tube sheet 5 so that the pore 5-1 of the 2nd tube sheet 5, 5-2, and 5-3 may be faced opening. Still more proper spacing on the left-hand side of a graphic display of said tube sheet 5 was vacated, and the 3rd tube sheet 9 is attached to idiosoma 1. And the pore 5-1 opened in the 2nd tube sheet, 5-2 and 5-3, the concentric pore 9-1, 9-2, and 9-3 are opened in this 3rd tube sheet 9. the end of the tubed heat exchanger tube 10-1 which is equivalent to opening of this pore 9-1, 9-2, and 9-3 at the container liner of a double pipe, 10-2, and 10-3 -- liquid -- it attaches densely. The other end of this heat exchanger tube 10-1, 10-2, and 10-3 is suitably estranged from the bottom of the heating tube 8-1 of the shape of said test tube, 8-2, and 8-3.

[0012] On the other hand, attach airtightly the header 11 for carbon-dioxide-gas recovery further to the right-hand side of the tube sheet 4 which fixed ceramic tubing, and [this header 11] The carbon-dioxide-gas outlet nozzle 11-1 into which carbon-dioxide-gas D which flows from the ceramic tubing 7 is made to flow is formed, it is open for free passage for this nozzle 11-1, and the carbon-dioxide-gas liquefier 16 is formed. moreover -- as opposed to the 3rd tube sheet 9 which installed the heat exchanger tube 10 -- the header 12 for heat carriers -- liquid -- it prepares densely. The inlet pipe 12-1 and outlet pipe 12-2 with which a heat carrier A flows are installed in this header 12 for heat carriers.

[0013] Next, the action of this example is explained. A heat carrier A comes from the outlet pipe 12-2 of the header 12 for heat carriers out of a system, flowing into the outer case heating tube 8 of the outside shape of a long and slender test tube, and heating the reforming catalyst layer 6, after flowing from the heat carrier inlet pipe 12-1, flowing into the container liner heating tube 10 of a double pipe and flowing in this. Moreover, combustion gas B which mixed methane and a steam goes into the 1st block P-1 of idiosoma 1 from the combustion gas inlet tubing 2, penetrates the 1st reforming catalyst layer 6-1, and goes into the 2nd block P-2. When combustion gas B penetrates a reforming catalyst layer, it causes the reaction shown by following [-ized 2] by work of a catalyst, generates hydrogen enriched gas, and also generates carbon dioxide gas simultaneously at this time.

[0014] [-izing 2]

CH₄+H₂O=CO+3H₂ (1) CH₄+2H₂O=CO₂+3H₂ (2 [0015]) In addition, since

refining of all the combustion gas that flowed in the reforming catalyst layer 6-1 is not carried out, unreacted combustion gas exists in the 2nd block P-2 besides hydrogen enriched gas and carbon dioxide gas. After these gas is heated from the heat carrier A which flows through a heating tube 8, it penetrates the 2nd reforming catalyst layer 6-2 further, causes the reaction of [-izing 2] in that case, and goes into the 3rd block P-3. Carbon dioxide gas is absorbed with the ceramic tubing 7-1 into which JIRUKONEITO was infiltrated in the 3rd block P-3.

[0016] [the ceramic tubing 7 into which this JIRUKONEITO was infiltrated] The gas containing carbon dioxide gas of a high pressure relatively [outside / of tubing] And when it is made to contact the gas which contains carbon dioxide gas of a low pressure relatively [inside / of tubing], The carbon dioxide gas which exists in the outside of tubing flows into the inside with a low pressure through the pore of Ceramics Sub-Division, and is brought together in the header 11 for carbon-dioxide-gas recovery through the inside of the ceramic tubing 7. The carbon dioxide gas brought together in the carbon-dioxide-gas header 11 is liquefied with the liquefier 16. Since a pressure becomes low relatively by liquefaction of this carbon dioxide gas in the direction inside the outside of the ceramic tubing 7, a methane reforming reaction equilibrium collapses and a reforming reaction is promoted.

[0017] Unreacted gas carries out the reaction shown by [-izing 2] whenever it penetrates the 3rd reforming catalyst layer 6-3 - the 6th reforming catalyst layer 6-6 henceforth, and it also generates carbon dioxide gas while it generates hydrogen enriched gas. Hydrogen-enriched-gas C with high purity is obtained, and it is taken out from the block P-7 of the last stage out of a system from an outlet pipe 3.

[0018] As stated above, while heating gas B advances a reforming reaction, according to the form of this operation, carbon dioxide gas is separable. Therefore, since a methane reforming reaction equilibrium collapses, a reforming reaction is promoted.

[0019] Like before, when not separating carbon dioxide gas, it is one condition for temperature to obtain about 800 degrees C or more of the greatest rates of refining to a reforming reaction, but temperature required for a reforming reaction can be made low by separating carbon dioxide gas. For example, refining which made the heat source about 600-degree C gas turbine exhaust gas can be performed.

[0020] Drawing 4 is the sectional view showing the 2nd embodiment of this invention. Drawing 5 is a sectional view which meets the V-V line of drawing 4 . heating tube 8' is U character type -- opening ends -- a tube sheet 5 -- liquid -- it is attached densely. The inlet pipe 12-1 and the outlet pipe 12-2 are formed in the heat carrier header 12. 13 is a diaphragm for dividing the inside of a header 12.

[0021] Drawing 5 is a sectional view when a V-V line cuts drawing 4 , and it is installed so that the reforming catalyst layer 6 may be inserted between U character type heating tube 8' and the ceramic tubing 7. The reforming catalyst layer 6 is joined to the tube sheet 4 and the tube sheet 5.

[0022] According to this embodiment, when heating tube 8' is a U tube format, the same effect as the case of the heating tubes 8 and 10 of hollow dual structure shown previously can be acquired.

[0023]

[Effect of the Invention] while it can process so that carbon dioxide gas leading to global warming may not be emitted according to this invention, and advancing the reforming

reaction of methane -- carbon dioxide gas -- separation -- ***** -- a methane reforming reaction equilibrium collapses and a reforming reaction is promoted by things. Furthermore, [in the case of the conventional technique in which carbon dioxide gas is not separated] although it was one condition for temperature to obtain about 800 degrees C or more of the greatest rates of refining to a reforming reaction In this invention, refining which there is an effect which makes this temperature low since carbon dioxide gas is separated, for example, made the heat source the gas turbine exhaust gas which is about 600 degrees C can be performed.

[Brief Description of the Drawings]

[Drawing 1] The sectional view showing the 1st embodiment of the carbon-dioxide-gas discrete type refining machine concerning this invention.

[Drawing 2] A is a sectional view which meets the II-II line of drawing 1 . B is the front view of a tube sheet 4. C is the front view of a tube sheet 5.

[Drawing 3] The top view showing the tubing edge of ceramic tubing of drawing 1 .

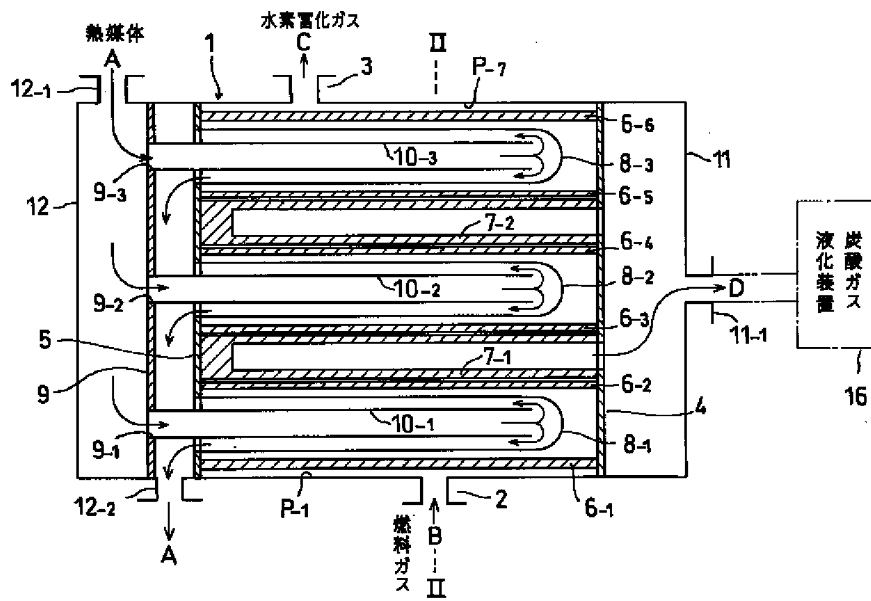
[Drawing 4] The sectional view showing other embodiments of this invention.

[Drawing 5] The sectional view in alignment with V-V of drawing 4 .

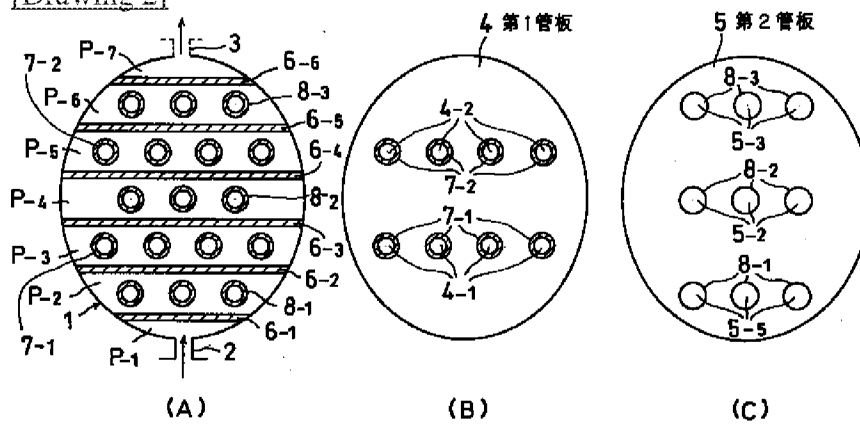
[Explanations of letters or numerals]

- 1 -- Body
 - 2 -- Combustion gas inlet tubing
 - 3 -- Hydrogen-enriched-gas outlet pipe
 - 4, 5, 9 -- Tube sheet
 - 6 -- Reforming catalyst layer
 - 7 -- Ceramic tubing
 - 8, 8, 10 -- Heating tube
 - 11, 12 -- Header
-

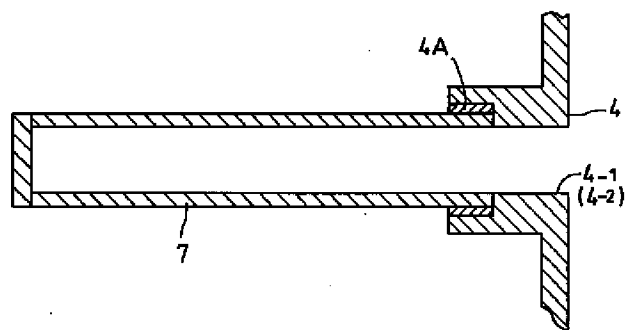
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Drawing 4]

